

## MANGANESE DIOXIDE FOR LITHIUM BATTERY CATHODES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is the national stage entry of International Patent Application No. PCT/UA2004/000057, filed on July 30, 2004, which claims priority to U.A. Patent Application No. 20031212437, filed on December 25, 2003.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not applicable.

FIELD OF THE INVENTION

[0003] The present invention relates to chemical power sources, and in particular to chemical power sources with lithium anode and non-aqueous electrolyte, in which manganese dioxide is used as an active cathode substance, with the objective of developing manganese dioxide to provide high efficiency for both primary and secondary Li-MnO<sub>2</sub> cells.

BACKGROUND OF THE INVENTION

[0004] In order to provide highly efficient and highly stable electrochemical characteristics for cathodes of lithium batteries based on MnO<sub>2</sub>, the MnO<sub>2</sub> must have specific properties. These properties can be achieved by using special processes for synthesis. As a result, the power sources based on this oxide would have desirable characteristics in both primary and rechargeable product applications.

[0005] Manganese dioxide for lithium power sources with a primary discharge capacity of 140mA·h/g 140mA·h/g (in terms of cathode substance) have been described. This capacity drops to 90.0 mA·h/g in the 300th cycle (A 3 volt lithium manganese oxide cathode

for rechargeable lithium batteries/Huang Haitao, Bruce Peter G., J. Electrochem. Soc..-1994/-141. #7.-CL76-L77).

[0006] A manganese dioxide with the discharge capacity during the first discharge of 150mA·h/g 150mA·h/g has also been reported. During repeated cycling the discharge capacity decreases below the 90.0 mA·h/g 90.0 mA·h/g (Investigation of lithiated manganese oxides as the materials for rechargeable cathode of lithium chemical power sources», N.I.Globa, E.M.Shembel, A.S. Strizhko. Abstract. The 3d Meeting on lithium power sources, Ekaterinobourg, October 4-7, 1994.- P.6).

[0007] The low discharge capacity of the  $MnO_2$  based cathode for the first discharge process and the characteristic instability of  $Li-MnO_2$  power sources during cycling are the disadvantages of the above mentioned  $MnO_2$  materials. .

[0008] The electrochemical method of manganese dioxide synthesis from electrolyte based on water solution has been described. During electrochemical synthesis the  $MnO_2$  is deposited on the anode surface. Manganese dioxide that is produced by the method of electrochemical synthesis is used as a cathode material in the different types of the chemical power sources: a) with none aqueous electrolyte and lithium anode; b) salt based aqueous electrolyte and a zinc based anode; c) alkaline based electrolytes and a zinc-based anode.

[0009] The main disadvantage of electrochemically synthesized manganese dioxide is its low tap density. As a result of the low tap density, cathodes based on electrochemically synthesized manganese dioxide have low specific discharge characteristics per volume, expressed in mA·h/cm<sup>3</sup> mA·h/cm<sup>3</sup>. As a result, the chemical power sources, which utilize cathodes based on electrochemically synthesized manganese dioxide, also have the low discharge characteristics on a per-volume basis.

[0010] The method of chemical synthesis for manganese dioxide is based on manganese nitrate oxidation by sodium chlorate in 30-32%- nitric acid at 85-90°C 85-90°C

followed by separation, washing and drying of the product deposit at 105-110°C. (Patent of FSU (USSR) № 1347353 of 10.09.85; MKI CO1G 45/02) is the closest to that of the present invention.

**[0011]** Disadvantages of MnO<sub>2</sub> produced by the methods mentioned above are as follows:

- non-serviceability in lithium power sources due to the crystallization moisture up to 5%, which is not removed under common conditions of treatment.
- low concentration of MnO<sub>2</sub> active substance (90-92) %
- low bulk density of the product; not more than 2.3-2.4 kg/dm<sup>3</sup>
- low conductivity of the product, equal to not more than 3.0 S/m (conductivity has been determined by the non-contact eddy-current method according US Patent Application 11/244,796).

#### SUMMARY OF THE INVENTION

**[0012]** An objective of the present invention is to improve the quality of the manganese dioxide and provide manganese oxide powder with high tap density (packing density) and high electronic conductivity, as well as high discharge capacity and more efficient cycling characteristics.

**[0013]** This objective is achieved in that the manganese dioxide of the present invention for the cathodes of lithium power sources is produced by manganese nitrate oxidation by sodium chlorate in a nitric acid medium. Oxidation is provided by heating followed by separation from the reaction mixture. After separation, the oxide is thermally treated. According to the invention, the nitric acid concentration during the MnO<sub>2</sub> synthesis is changed from 38-44% at the beginning and up to 23-26% at the end of the synthesis process. After the synthesis, thermal treatment of the product is carried out in air at 240-

320°C. The structure of manganese oxide is according to the present invention can be characterized by the formation in the diffraction as comprising an x-ray phase diffraction as comprising a mixture of the  $\gamma$  and the  $\beta$  phases.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The manganese dioxide produced based on the synthesis method described in the current invention has considerable advantages as compared with known prior manganese dioxide. Due the special condition of the synthesis, including:

the change of the nitric acid concentration during the synthesis, such as from 38-44% at the beginning and up to 23-26% at the end of the synthesis process, and special regime for treatment of the oxide in air at 240-320°C after synthesis.

[0015] The resulting manganese oxide has properties that favorably influence its electrochemical characteristics.

[0016] Manganese dioxide synthesized according this method has a bulk density of 2.5-2.9 kg/dm<sup>3</sup> with integral particle distribution in the range 1-3 up to 60-70  $\mu$ m. The ratio between a bulk density (in kg/L<sup>2</sup>) and specific surface (m<sup>2</sup>/g) of manganese dioxide is in the range of 0.08 – 0.40. The quantity of the pure total mass of MnO<sub>2</sub> in the oxide is 94.0-96.0%. The structure of the manganese oxide corresponds to the formation of the x-ray phase mixture of the  $\gamma$  and the  $\beta$  phases. The effective electronic conductivity of the MnO<sub>2</sub> powder synthesized according the present invention is at least 3.4 S/m. Conductivity has been measured using the eddy-current non-contact testing at the frequency 120kHz (US Patent Application 11/244,796).

[0017] The density of the cathode mass based on manganese dioxide synthesized according the present invention is 2.7 – 2.9 g/ cm<sup>3</sup>. In non-aqueous electrolyte, the cathode

discharge capacity at the first discharge is 270 mA·h/g in terms of the manganese dioxide. Upon cycling, the average discharge capacity is up to 170 mA·h/g.

[0018] Described below are the reasons why the characteristic of the manganese oxide of the current invention is important. The excellent characteristics of the manganese oxide synthesized according the method of current invention, and characteristic of cathodes based on this manganese oxide characteristics are determined by the following:

[0019] For manganese dioxide bulk density of less than 2.5 kg/dm<sup>3</sup> and the ratio between bulk density and specific surface less than 0.08, the following negative effects are evident:

1. For manganese dioxide bulk density of less than 2.5 kg/dm<sup>3</sup> and the ratio between bulk density and specific surface less than 0.08, the following negative effects are evident:

- cathode mass has the low level of the density (less than 2.0 kg/dm<sup>3</sup>), the structure of the manganese oxide powder affects the macrostructure of electrode. As a result, the electrode macrostructure is formed in such a way that primary discharge capacity is low. With such electrode macrostructure it is also impossible to achieve an effective charge process. As a result, the cycling of the power source is not practical. That is, the resulting microstructure leads to a sharp decrease in discharge capacity during cycling.

2. For manganese dioxide bulk density of greater than 2.9 kg/dm<sup>3</sup>, and the ratio between a bulk density and specific surface greater than 0.4, the following negative effects are evident:

- cathode mass is slightly granulated thus preventing the fabrication of high-quality cathodes.

3. When the fraction of total mass of manganese dioxide is less than 94% and conductivity less than 3.4 S/m, the following negative effects show themselves because of

insufficient removal of crystallization moisture from a product and the primary prevalence of  $\gamma$ -MnO<sub>2</sub>:

- primary discharge capacity of cathode decreases;
- cathode cyclability decreases sharply;
- discharge voltage value decreases.

4. When the fraction of manganese dioxide total mass is more than 96% the following negative effects, due to product transition into the passive  $\beta$ - MnO<sub>2</sub> structures, take place :

- primary discharge capacity of cathode decreases,
- sharp drop of cyclability occurs.

[0020] The synthesis method for manganese dioxide of the present invention preferably changes the nitric acid concentration from 38-44% at the beginning of the synthesis process up to 23-26% at the end. The subsequent mode of thermal treatment enables production of manganese dioxide powder with an integral set of the particles from 1-3 up to 60-70 $\mu$ m. The ratio between a bulk density in (kg/dm<sup>3</sup>) and manganese dioxide specific surface (m<sup>2</sup>/g) is in the range of 0.08-0.40. The concentration of manganese dioxide is 94-96%, with the efficient conductivity of manganese dioxide powder as measured by an eddy-current method at a frequency of 120 MHz, of at least 3.4 S/m. This provides good discharge characteristics of batteries made with cathodes based on this material. To more clearly describe the present inventions, the following specific non-limiting examples are provided.

**Example 1.**

[0021] 0.4-0.8dm<sup>3</sup> of 38-44% nitric acid is was placed into titanium reactor with the volume up to 1dm<sup>3</sup> overflow with a mechanical agitator. The manganese nitrate solutions are were measured at 80-100°C. A reaction mixture comprising solid manganese dioxide is was

removed through the overflow into a separate container and filtered. The process is carried out until the nitric acid concentration in the reaction mixture is equal to 23-26%. The filtered product is was washed to neutralize nitric acid residue, and dried at 105-140°C. In this case, bulk density of the produced powder is 2.5-2.9 kg/dm<sup>3</sup> with the integral particle distribution ranging was found to range from 1-3 up to 60-70 µm.

**Example 2.**

[0022] Manganese dioxide, as produced in Example 1, was then thermally treated at 240-320°C until the manganese dioxide content was 94-96%. In this case, the powder form conductivity, as measured by the method of eddy-current as described in published U.S. Patent Application No. 20060127267 to Redko et al., was performed at a frequency of 120 MHz (~~MPK7 G01N 27/02,27/06,27/22 № 54354A published 17.02.03. Bull. № 2~~) is and revealed a conductivity of at least 3.4 Sm/m.

**Example 3.**

[0023] Manganese dioxide powder as produced above is was mixed with a conducting additive as a mixture of carbon black and graphite. The binder PTFE or PVdF is was added to the slurry. The resulting cathode mass is was deposited onto a stainless steel, aluminum or titanium grid or foil. The resulting cathode mass density is was found to be 2.7-2.9 g/ cm<sup>3</sup>.

[0024] The resulting cathode can be used in primary and secondary lithium power sources. This is illustrated by the example below.

**Example 4.**

[0025] After drying, the cathode produced in accordance with the Example 3 is was placed into non-aqueous electrolyte, where cathodes are tested and discharge capacity and discharge voltage are measured. The measurements are carried out in a three-electrode cell, where the investigated electrode based on manganese dioxide is was used as a working

electrode, and lithium electrodes serve as auxiliary and reference electrodes. During cathode discharging, the capacity at the first cycle is ~~270 mAh/g~~ 270 mA·h/g. For the second and subsequent 80 discharge cycles, discharge capacity ranges from 170 to ~~145 mAh/g~~ 145mA·h/g.

**[0026]** Data from these examples are summarized by the results shown in Tables 1 and 2 below:

Table 1.

№	Bulk density of MnO <sub>2</sub>	Relation between bulk density and specific surface	Fraction of MnO <sub>2</sub> total mass (%)	Conductivity (S/m)	HNO <sub>3</sub> concentration at synthesis	Discharge cathode capacity, mA·h/g (in terms of MnO <sub>2</sub> )				Note		
						initial	final	1 <sup>st</sup> cycle	2 <sup>nd</sup> cycle	10 <sup>th</sup> cycle		
1	2	3	4	5		6	7	8	9	10	11	12
1	2.5	0.32	95	3.5	44	23	260	170	160	145	Claimed manganese dioxide properties	
2	2.7	0.12	95	3.5	42	25	270	190	170	155	The same	
3	2.9	0.26	95	3.5	41	25	255	160	150	145	The same	
4	2.4	0.21	95	3.5	42	24	220	110	90	75	Low discharge capacity; bulk density of the product is lower than the claimed limit	
5	3.0	0.09	95	3.5	43	25	210	110	90	70	Low discharge capacity; bulk density of the product is higher than the claimed limit	
6	2.7	0.07	95	3.5	43	25	225	120	100	90	Low discharge capacity; ratio between bulk density and specific surface is lower than the claimed limit	
7	2.7	.5	95	3.5	40	24	215	105	90	70	Low discharge capacity; ratio between bulk density and specific surface is higher than the claimed limit	

### Continuation of Table 1.

[MARKED-UP VERSION]

TABLE 2

Temperature of thermal treatment	X-ray phase composition	Manganese dioxide content (%)	Specific capacity of the 1 <sup>st</sup> cycle, mA·h/g	Specific capacity at cycling, mA·h/g
200	$\gamma$ - MnO <sub>2</sub>	94	240	150
250	$\gamma$ , $\beta$ - MnO <sub>2</sub>	95	270	180
300	$\gamma$ , $\beta$ - MnO <sub>2</sub>	95	270	180
350	$\beta$ - MnO <sub>2</sub>	94	230	120

[0027] As illustrated in the above examples and data tables, manganese dioxide with the characteristics described enables production of the cathodes with excellent discharge characteristics in both the primary and rechargeable lithium chemical power source with non-aqueous electrolyte.

CLAIMS

**We claim:**

1. Manganese dioxide for cathodes of lithium power sources, produced by manganese nitrate oxidation by sodium chlorate in nitric acid media with heating followed by separation from reaction mixture and thermal treatment characterized in that nitric acid concentration in the synthesis process is changed from 38-44% at the beginning and up to 23-26% at the end of the process, with bulk density of the manganese dioxide being 2.5-2.9 kg/dm<sup>3</sup> with integral particle size distribution in the range of 1-3 up to 60-70 µm, and its efficient conductivity is at least 3.4 S/m.
2. Manganese dioxide as in Claim 1, characterized in that a ratio between bulk density in (kg/dm<sup>3</sup>) and specific surface (m<sup>2</sup>/g) of said manganese dioxide is in the range of 0.08 – 0.40.
3. Manganese dioxide as in Claim 1, wherein its treatment is carried out in air at 240-320°C until the manganese dioxide has a concentration of 94-96% with simultaneous formation the of an x-ray phase mixture of  $\gamma$  and  $\beta$  phases.
4. Manganese dioxide in Claim 1, wherein the a mass density of cathodes based on said manganese dioxide is 2.7-2.9 g/cm<sup>3</sup>.

5. Manganese dioxide as in Claim 1, wherein the primary discharge of cathodes ~~maid~~ made from said manganese dioxide, in non-aqueous electrolyte, has a discharge capacity of up to ~~270 mA·h/g~~ 270 mA·h/g in terms of manganese dioxide.

6. Manganese dioxide as in Claim 1, wherein cycling ~~the~~ a cathode made from said manganese dioxide in non-aqueous electrolyte ~~have~~ provide a discharge capacity of ~~up~~ 90 to 170 mA·h/g in terms of manganese dioxide.

ABSTRACT

The present invention relates to chemical power sources, in particular to chemical batteries provided with a lithium anode, and an oxide based cathode with a non aqueous electrolyte. In this type of battery the manganese Manganese dioxide is used in the form of for an active cathodic agent. The manganese dioxide is synthesized by oxidizing a manganese nitrate by a sodium chlorate in a nitric acid associated with heating, subsequent separation of a product from a reaction medium and heat processing. The concentration of the nitric acid is modified from 38-44 % at the beginning of synthesis to 23-26 % at the end thereof. The content of the thus produced manganese dioxide is equal to 94-96 %, a bulk density thereof ranges from 2.5 to 2.9 kg/dm<sup>3</sup>, the particle size distribution ranges from 1-3 to 60-70 microns, and the electric conductivity is equal to, or greater than, 3.4 S/m. The inventive active cathode material exhibits a high discharge capacity and cycling capacity under commonly encountered operating conditions. The present invention makes possible to use said material for lithium primary and multi charge batteries.